

## INVESTIGATIVE STUDIES ON ACTUAL PLUME BEHAVIOR RELATIVE TO PREDICTED VALUES DURING SPILL EPISODE INVOLVING LIGHT NON-AQUEOUS PHASE LIQUIDS (LNAPL)

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### Abstract

Groundwater and soil contaminations phenomena are two of the most recent environmental issues today. Due to various anthropogenic activities, the ground surface and the soil underneath are subject to inevitable contaminations. The groundwater resources, the soil and the dependent terrestrial ecosystems are the targets of impacts due to underground spillage of petroleum oils, one of which is the Light Non Aqueous Phase Liquids or LNAPL. The particle LNAPLs that may volatile to the ground surface could endanger the health of the people thriving on lands directly above the impact area. Due to spillage, bioaccumulation of the substance via the deep rooted plants could pose threats to health of their consumers. The chain effects are varied and so therefore an accurate analysis should be done to understand their most probable behavior and remediation. In the petroleum spill incident investigated in this paper, approximately a million liters of fuel has been spilled resulting from a damage pipeline used to convey various petroleum products from the refinery to a central depot in the city center, an atypical plume behavior of the contaminant was observed characterized by increasing and decreasing plume area. This phenomena could be related to the suggested hypothesis as observed by hydrologist in the research work of Marinelli and Durford (1996). The effect of the rising and falling of the water table in the site and the sorption to the soil particles of LNAPL may have inferred in the contraction of the plumes demonstrated in the results of the wells monitored within the site. In addition, the remediation implemented to the site, the multi-phase extraction (MPE) system, could have contributed significantly to this phenomenon of plume contraction. After sometimes, the observed monitoring wells were decommissioned and the hydrocarbon recoveries were terminated. With still an approximate million liters of contaminating fuel present underground of the contaminated area of Barangay Bangkal, Makati City, in which most of the free fuels phase (PAH) lying beneath the nearby South Expressway in Makati area, several monitoring wells were closely monitored in order to determine the still available BTEX using Gas Chromatograph Mass Spectrometer. Extensive well monitoring data complemented by modeled data were used to explain the phenomenon. The effect of the rising and falling of the water table in the site and the sorption to the soil particles of LNAPL are seen as the most probable reasons for the contraction of the plumes. Moreover, heavy water withdrawals from the Multi-Phase Extraction System (MPE) used in the remediation process contributed significantly as shown in model results using MOFAT and validated with actual data from the site.

**Keywords:** multi-phase extraction (MPE) system, light non-aqueous phase liquid (LNAPL), plume, sorption, MOFAT

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### 1.1 INTRODUCTION

In 12 July 2010, Light Non-Aqueous Phase Liquid (LNAPL), also known as phase-separated hydrocarbon (PAH), was discovered by residents of West Tower condominium in Bangkal, Makati in the level two of its basement. Due to the unusual smell and chemically dangerous vapors of this gas, the local government of Makati City advised them to vacate the area on 23 July 2010. West Tower Condominium has four basement levels below ground surface in which the deepest is at approximately 13.5 mbgs (meters below ground surface). In this part of the basement is where the voluminous quantity of groundwater extracted with LNAPLs. The accumulated hydrocarbon vapors that volatilized and confined within the basements of the building posed health risk and dangerous possible explosion.

### 1.2 Statement of the Research Problem

The approximate 2,000,000 liters of petroleum oil that leaked in the First Philippine Industrial Corporation (FPIC) underground pipe line identified in the street of Brgy. Bangkal, Makati City posed a major environmental threat. With the joint efforts of the Makati City government, FPIC, CH2M Hill and the UP NIGS, the planned clean-up had eased the burden of fuel substances. However, the predictability of time when the contaminant BTEX will be below its regulated level is being strived hardly to be resolved using the MPE (purging extraction wells) technology.

The issue about these observations were raised and a question was asked as to where did the approximate one million liters go when groundwater had risen up its level due to precipitations? The following hypotheses were conceived:

1. Fuel was dissolved by added volumes of groundwater and spread laterally (UP NIGS)?
2. Fuel “hid” beneath the water column (CH2M HILL)?

### 1.3 Objective

This study aims to meet the following objective: To provide an explanation on the actual plume behavior relative to the predicted values during spill episode involving light non-aqueous phase liquids (LNAPL).

### 1.4 Specific Objectives

- 1.) To provide an explanation of the increased water table due to precipitation and the corresponding decreased plume behavior of a multi component LNAPL in Bangkal, Makati City spill incident.
- 2.) To compare and analyze the actual plume behaviors with the theoretical results of the Software Application MOFAT.
- 3.) To estimate the remaining volume of LNAPL in the site and provide possible clean-up time frame under a business as usual scenario i.e. using MPE system.
- 4.) State the predicted values using the software in order to validate the result.
- 5.) Describe the spill episode by citing some specific data regarding the event.

### 1.5 Background of the Study

The first quarter of 2012 marked the construction of the multi-phase extraction (MPE) system by a private consultant of the local government of Makati City to address the incident of groundwater contamination in Barangay Bangkal. This pipeline spills over the area was detected in October 2010 and after extraction efforts, approximately one million liters still need to be recovered or decontaminated from the ground out from an approximately 1.8 million liters of oil spills. Contaminants plumes were already drafted describing the behavior of the LNAPL substance using the data from the 45 monitoring wells that were established around the area. In this proposed study, the clarification of the issue regarding the observations that were raised and a question which was critically asked as to where do the one million liters go when groundwater increased due to precipitations. The following hypotheses were conceived by the commissioned consultants: 1) Fuel was dissolved by added volumes of groundwater and spread laterally (UP NIGS), 2) Fuel “hid” beneath the water column (CH2M HILL).

As what Marinelli and Durnford (1996) had noted, four common observations that field hydrogeologists made as hydrocarbon spill sites and offered explanations for each that are related to the *rise and fall of water table*, which could possibly had taken place in the Bangkal Makati oil spill incident. A wide variety of materials were identified as contaminants found in groundwater. These include synthetic organic chemicals, hydrocarbons, inorganic cations, inorganic anions, pathogens and radionuclides. Most of these materials will dissolve in water to varying degrees. Some of the organic compounds are only slightly soluble and will exist in both a dissolved form and as an insoluble non-aqueous phase, which can also migrate to the ground (Fetter, 2<sup>nd</sup> Ed.). The natural tendency of many non-gaseous chemical substances that leaked to the soil has to go to the ground via gravity and soil matric potential. In the process, consequent physical, biochemical and chemical phenomena will take place to the contaminants before they find their way to their final destinations. Chemical and biochemical reactions may transpire and convert some portions of these substances into other chemical forms while leaving the remaining amount to the various physical phenomena in air, soil and water. The fate of most Light Non-Aqueous Phase Liquids (LNAPL): gasoline and diesel fuel, benzene, toluene, xylene, and hydrocarbons are normally found in the top soil surface where a leak had taken place, in the vadoze zone of the soil where multi-phase flow can happen and into the groundwater. Most petroleum hydrocarbons have a low *octanol-water partition coefficient*; therefore they migrate easily through soil columns and reach groundwater aquifers.

Most petroleum hydrocarbons are toxic to water and soil and thus interfere with their uses. One attractive approach for remedying a contaminated aquifer is an ex-situ technique in which water is pumped out of the aquifer (i.e. purging wells, MEP) and subsequently treated for target contaminants. Some techniques have been investigated for the removal of hydrocarbons from contaminated water, including

biodegradation, adsorption onto activated carbon; membrane processes; and advance oxidation processes (Moussavi et al., 2011).

In cleaning up LNAPL spills, the mobile LNAPL can be removed by skimming wells or trenches. However, a considerable amount of LNAPL will be left as a residual in soil. Volatile LNAPLs can be removed by soil-vapor extraction system. However, nonvolatile products will remain behind in the soil. The amount depends upon the properties of the LNAPL and the texture of the soil. The oil retention capacity of soil is estimated to range from 5 L/m<sup>3</sup> for gravel to 40 L/m<sup>3</sup> for silty sand (Testa and Pacskawski 1989).

Many hydrocarbons can be degraded by soil bacteria, especially if the soil is aerobic. Systems that diffuse air into the soil have been effective in bioremediation of hydrocarbon spills. Biological research was also conducted to find a fast and accurate solution in reclaiming a petroleum oil-contaminated soil which turned out to be unsuitable for the cultivation of crops. Mukherjee and Bordoloi suggested in their experiment the introduction of microbial consortium such as *Bacillus subtilis* DM-04 and *Pseudomonas aeruginosa* M and NM strains to treat petroleum contaminated soil under the conditions ideal to the said microorganisms (Mukherjee & Bordoloi, 2010).

## 1.6 The Actual Oil Spill Event in Barangay Bangkal, Makati City, Philippines

First Philippine Industrial Corporation (FPIC), which was established in 1967, installed and maintains the only and largest commercial pipeline in the Philippines. These pipelines transport crude and refined petroleum products from Batangas to Pandacan Depot in Metro Manila. FPIC pipeline system consists of two main classifications, one for the refined petroleum products (the “white” line) and for the heavier petroleum products (the “black” line). It primarily supplies the fuel requirement of Manila Electric Company (Meralco) via the Pandacan depot in the city of Manila and the oil refineries in Batangas. The company is owned by First Holdings, in partnership with Shell Petroleum Co., Ltd. (UK). In 1992, the Energy Regulatory Board renewed FPIC’s concession to operate its pipelines for another 25 years.

In July 2010, oil seeped into the basement of 22-story West Tower Condominium in Barangay (village) Bangkal in Makati City alarming residents in the area. The leak was eventually traced to 5 rice grain-sized holes in a portion of the 117 kilometers pipeline operated by First Philippines Industrial Corporation (FPIC) just meters away from the condominium (Philippine Daily inquirer, Thursday, January 10<sup>th</sup>, 2013).

In 12 July 2010, Light non-aqueous phase liquid (LNAPL) also known as phase-separated hydrocarbon (PAH) was discovered by residents of the condominium in the level 2 of its basement. Due to the unusual smell and chemically dangerous vapors of this gas, the local government of Makati City advised them to vacate the area on 23 July 2010. West Tower Condominium has four basement levels below ground surface which the deepest is at approximately 13.5 mbgs (meters below ground surface). In this part of the basement is where the most voluminous sump of the area drawing groundwater with LNAPL through the soil towards the building. West Tower Condominium management engaged BENSAN Industries Inc. (BENSAN) to recycle used oil and extract LNAPL-water mixture in the basement. Using oil-water separator and extracted some 322,000 liters (1,610 drums) of LNAPL-water mixture stored in 200 liter drums (CH2M HILL).

In 9 December 2010, FPIC in a press correspondence informed the media that about 9,000 drums or 1,800,000 liters of petroleum product may have leaked from their pipe.

CH2M HILL Philippines, Inc., was commissioned by First Philippine Industrial Corporation (FPIC) to conduct an, “Environmental Site Assessment” (ESA) of the identified surface and sub-surface condition for the site defined by the following streets: Gen. Garcia A. Apolinario, A. Bonifacio, Osmeña Highway, and encompassing primarily the West Tower Condominium (West Tower) at Gen. del Pilar Street and Gen. Garcia Street and Osmeña Highway, Barangay Bangkal, Makati city, Philippines. The study area includes portions of the fuel pipeline operated by FPIC along the southbound portion of Osmeña Highway within Makati (see Figure 3). Fieldworks were conducted by CH2M HILL to delineate the plume of the dissolved LNAPL in the subsurface geology of the area.

Since the Philippines has no specific standards governing the remediation of petroleum contaminated sites, so the Inter-Agency Committee on Environmental Health (IACEH) had adopted the standards used by United States Environmental Protection Agency (US EPA). The agency has approved the FPIC’s proposed system for the recovery and treatment of petroleum leakage from their pipeline which affects West Tower and Barangay Bangkal. In a resolution issued dated October 14 2011 and signed by then Health Secretary Enrique Ona, IACEH Chairman, the committee approved the multiphase extraction (MPE) technology that

FPIC proposed for its remediation efforts in the affected area. Moreover, the technology was approved by the Environmental Technology Approval (ETA) of the Department of Science and Technology's Industrial Technology Development Institute (DOST-ITDI). In a statement, FPIC said ITDI Director Nuna Almanzor endorsed the MPE (Philippine Daily Inquirer – December 9th, 2011).

The West Tower basement is the deepest structure in the area, and apparently has a constructed drainage system in the exterior wall. The maintenance by pumping to permanently dry-up the basement area had incidentally withdrawn groundwater with petroleum oil. The groundwater with contaminant was collected in the fourth level basement, withdrawn and was contained to be treated. Due to the substantial withdrawals, it was approximated that a million liters of petroleum gas were extracted from the basement of West Tower Condominium.

According to the University of the Philippines National Institute of Geological Sciences (UP NIGS), the first quarter of 2012 (January-March 2012) started the construction of the *multi-phase extraction* (MPE) system by FPIC-CH2M HILL. MPE system is capable of removing separate phase product (free product) from the sub surface, thereby reducing concentrations of petroleum hydrocarbons in both the saturated and unsaturated zones of the subsurface. This was designed to extract the petroleum oil in the groundwater and elutriates the soil as a result of the pipeline spill detected in the area on October 2010. The Makati Government consultants followed closely the construction plans, including monitoring of several monitoring wells that had to be decommissioned in order to give way to the purging wells of the MPE System. When the construction of the MPE started, the recovery efforts of hydrocarbons from wells were terminated from the sub surface. (Bangkal Contamination Consultants Report, January-July 2012).

## 1.7 Findings and Environmental Conditions

The following are the significant findings and environmental conditions as of July 2012 according to Bangkal Contamination Consultants Report by UP-NIGS:

1. Approximately 1 million liters of contaminating fuel are still present beneath the Bangkal area which most of the PAH is under the South Expressway.
2. Due to the consistent pumping done in the vicinity, it resulted to the absence of PAH in the monitoring wells around the West Tower. However, the fuel contaminating the soil and dissolved in groundwater still needs to be treated for PAH using MPE system.
3. It was also confirmed that there is no more leak coming from the pipeline near the Bangkal area, this is shown by the constant and even decreasing contaminant plume over time and also by the pressure testing conducted by the Makati City consultants. If leaks continue then there should be increasing size of the contaminant plume and evidence will be detected in the monitoring wells too.
4. The *multi-phase extraction* (MPE) system continued operation and the close monitoring of the system is being done for its efficiency. It was discharging more than 200,000 liters of treated water per day in Bangkal creek.
5. The National Institute of Geological Sciences University of the Philippines, Diliman had set up the latest Gas Chromatograph Mass Spectrometer. This is basically intended to detect the presence of carcinogenic BTEX in the contaminant. Its accuracy could handle the minute 5ppb of BTEX contaminant concentration. For benzene, the US EPA limiting standard for drinking water is 5µg/L.
6. The technical working group of the IACEH agreed that the level to which FPIC must restore the groundwater in Bangkal is <5ppb, based from US EPA standards. If those traces of BTEX contaminants in Brgy. Bangkal are still above the threshold limit of 5 ppb, groundwater treatment must continue and it was approximated to take years.
7. UP NIGS research team had committed to the people of Brgy. Bangkal that they will consistently monitor the development of the decontamination.
8. UP NIGS had participated with the Supreme Court proceedings on determining the integrity of the pipelines by pressure testing, employing the independent and internationally practicing pipeline professionals to vet the pressure testing process. After the standard procedures and evaluation of the results, the study team was convinced that pipelines are now leak free.
9. UP-NIGS research team recommended that all existing patches in the pipeline be repaired and/or be replaced for leak prevention.
10. They were also in agreement that the portion of the pipeline located beneath the expressway be realigned away from the expressway itself to avoid traffic-related stresses.

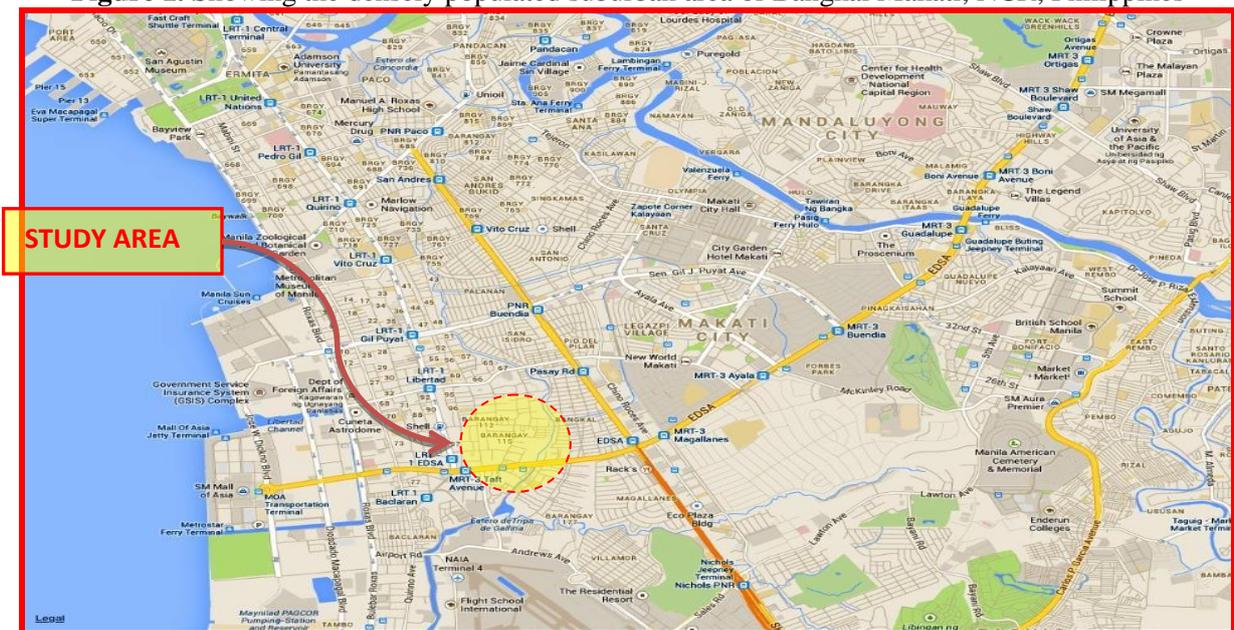
11. Based from the submitted result of the GCMS testing of the MPE and the monitoring wells for dissolved BTEX, the results suggest that the MPE system is working.
12. UP NIGS study team also found out that the area contaminated with BTEX, according to their findings, appeared to be bigger than the area determined by CH2M HILL study team.

### 1.8 The Study Area

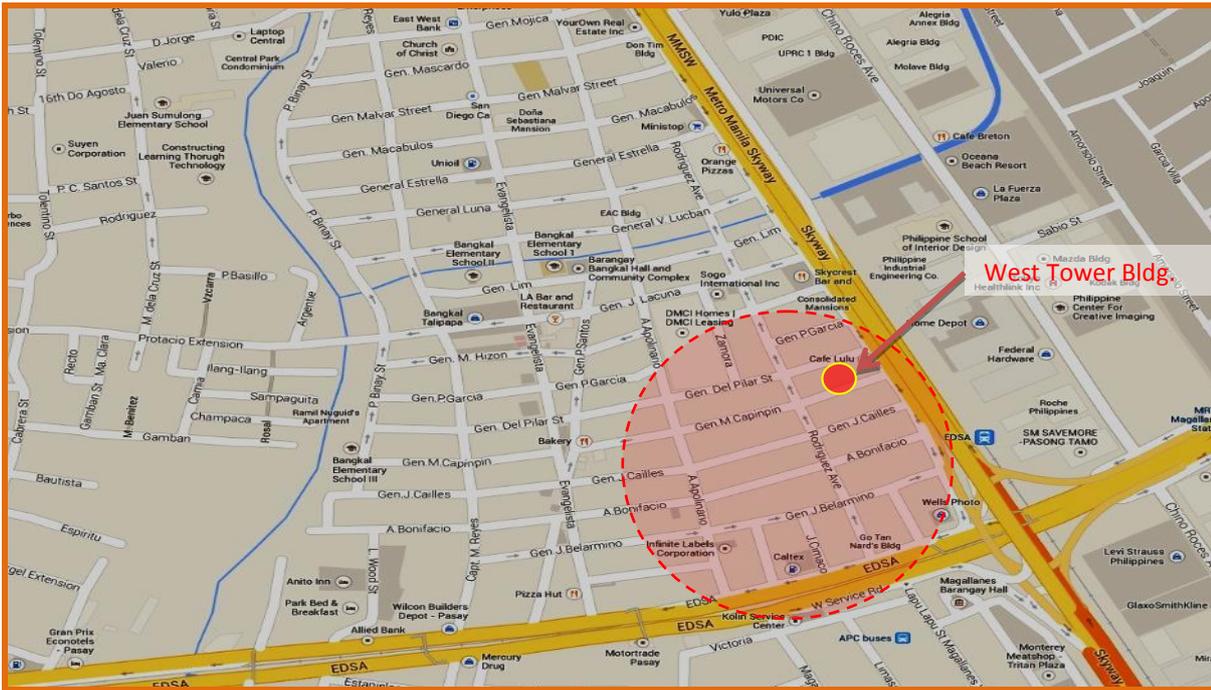
The study area includes portions of the fuel pipeline operated by FPIC along the southbound portion of Osmeña Highway within Barangay Bangkal, Makati



**Figure 1.** Showing the densely populated suburban area of Bangkal Makati, NCR, Philippines

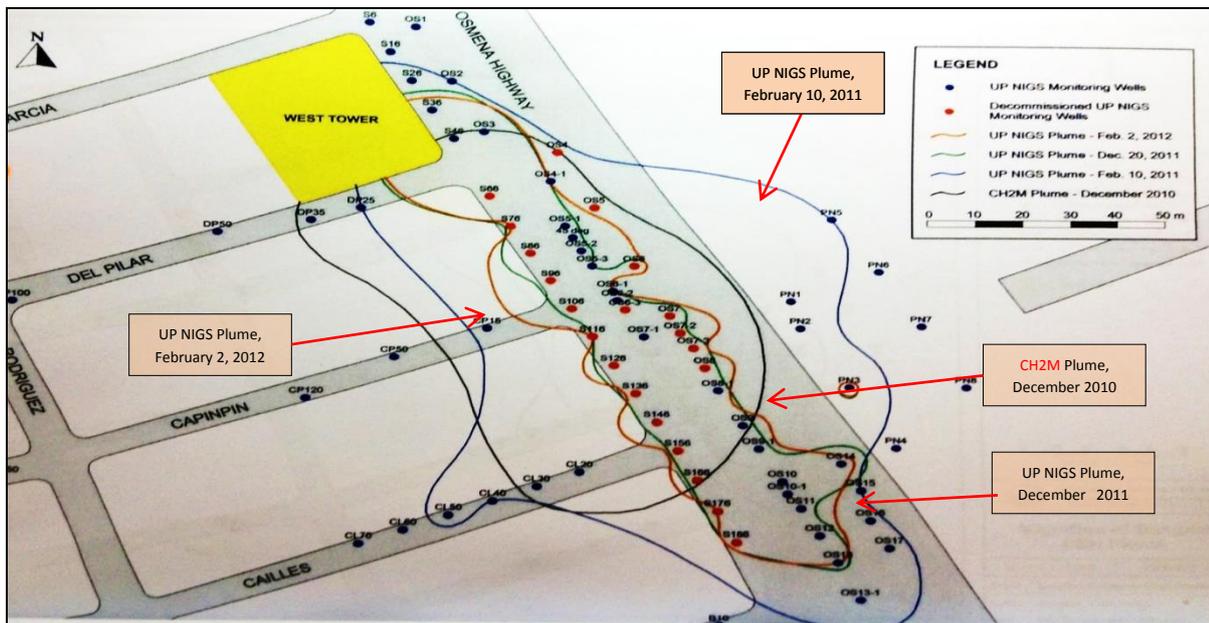


**Figure 2.** Shown is the map of Bangkal Makati where the LNAPL spill incident took place. It can also be seen in the map, the river systems near the area.



**Figure 3.** The study area and the streets within the vicinity.

### 1.9 The Contaminant Plumes

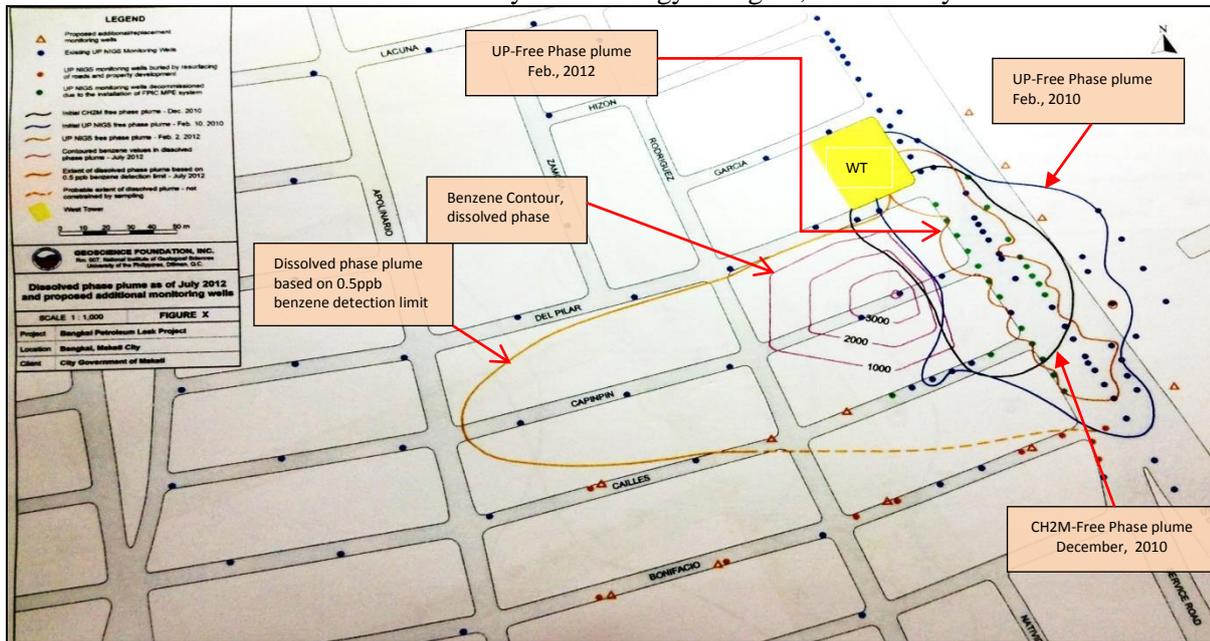


**Figure 4.** The contaminant plume behavior as observed by UPNIGS and CH2HILL's independent studies in Barangay Bangkal, Makati City

SOURCE: GEOSCIENCE FOUNDATION INCORPORATED, UP NIGS

The above pictures of contaminant plumes at different dates by the two consulting agencies showed decreasing areal shapes. UP NIGS observation dated 10 February 2011 (in blue) is seen to be the largest in areal shape, then it contracted after 10 months (see plume in green). Two months thereafter, another plume (in orange) contractions happened. CH2M plume (in black) was observed 2 months earlier than UP's first plume (in blue) observation but it can be observed that the areal size of the contaminant plume had expanded. The blue dots are the points of monitoring wells with their corresponding ID names established by UP study team. The orange dots are the monitoring wells constructed by CH2M HILL. It is also evident that UP had established much monitoring wells than CH2M.

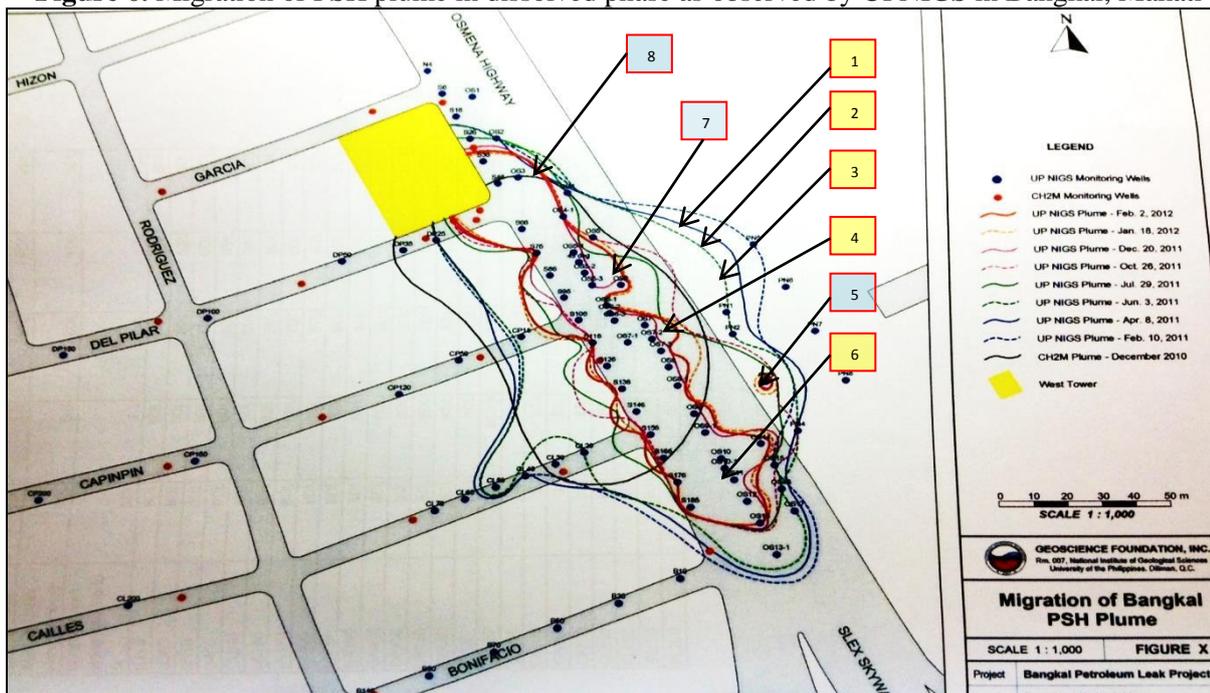
**Figure 5.** The contaminant plume behavior with contoured benzene values in dissolved phase as observed by UPNIGS study team in Brgy. Bangkal, Makati City



SOURCE: GEOSCIENCE FOUNDATION INCORPORATED, UP NIGS

Benzene concentration in ppb was detected in the different monitoring wells with the following ID name: CP15, CP120, CP150 and CP200 respectively. These monitoring wells have the following benzene concentrations: 151, 4,233, 2.7 and 1.2 ppb respectively (based from UPNIGS). The benzene concentrations were shown in the benzene contour illustrated in Figure 5. Dissolved phase plume based on 0.5ppb benzene detection limit was also shown in Figure 5. According to the technical working group of the IACEH, it was agreed that the level to which FPIC must restore the groundwater in Bangkal is <5ppb, based from US EPA standards.

**Figure 6.** Migration of PSH plume in dissolved phase as observed by UPNIGS in Bangkal, Makati City.



SOURCE: GEOSCIENCE FOUNDATION INCORPORATED, UP NIGS

The chronology of contaminant plumes behavior as observed by UPNIGS study team:

In Figure 6 above, the blue colored boxes are pointing to plumes that increased in areal shape. Plume no. 5, 7 and 8 became a little bigger in areal shape instead of following the sequence of contraction to smaller plume sizes.

1. February 10, 2011	1
2. April 8, 2011	2
3. June 3, 2011	3
4. July 29, 2011	4
5. October 26, 2011	5
6. December 20, 2011	6
7. January 18, 2012	7
8. February 2, 2012	8

All the rest of the plumes technically follow the norm of plume contraction based on the chronological order of observation. This may implies that the concentration of the LNAPLs had depleted due to continuous MPE application. For the plumes no. 5, 7, and 8, the possible increases in plume areal size could be attributed in the hydrogeological phenomena in the site's underground. The recharge due to precipitation that caused dissolution and as influenced by the groundwater level fluctuation may have influence this expansion of plume size.

#### FREE FUEL PLUME HISTORY

The date they were monitored and at a 20% rock porosity soil condition.

1. March 10, 2011 - 2,066,000 liters
2. June 3, 2011 – 1,820,000 liters
3. June 25, 2011 – 253,500 liters (after heavy rain)
4. October 26, 2011 – 475,000 liters
5. December 3, 2011 – 362,606 liters

An issue about these observations were raised and a question was asked as to where did the 1 million liters go when groundwater increased due to rains? The following hypotheses were conceived:

1. Fuel was dissolved by added volumes of groundwater and spread laterally (UP NIGS)?
2. Fuel “hid” beneath the water column (CH2M HILL)?

Water table fluctuations resulted in LNAPL and air entrapment below the water table, an increase in the vertical extent of the LNAPL source zone, and an increase in the volume of water passing through the source zone (Dobson, Chroth Zeyer 2007).

#### CONCLUSION

Extensive well monitoring data complemented by modeled data were used to explain the phenomenon. The effect of the rising and falling of the water table in the site and the sorption to the soil particles of LNAPL are seen as the most probable reasons for the contraction of the plumes. Moreover, heavy water withdrawals from the Multi-Phase Extraction System (MPE) used in the remediation process contributed significantly as shown in model results using MOFAT and validated with actual data from the site.

#### REFERENCES

- Barry, D.A., 1992. Modelling Contaminant Transport in the Sub-surface: Theory and Computer Programs. In: Ghadiri, H., Rose, C.W. (Eds.) Modeling Chemical Transport in *Soil: Natural and Applied Contaminants*. Lewis Publishers, Boca Raton, Florida, pp.105-144
- Dobson, R., Schroth, M. and Zeyer, J., 2007. Effect of Water-table Fluctuation on Dissolution and Biodegradation of a Multi-Component, Light Non Aqueous-Phase Liquid. *Journal of Contaminant Hydrology* 94 (2007) 235-248
- Falta, R.W., Rao, S.P., and Basu, N., 2004. Assessing the Impacts of Partial Mass Depletion in DNAPL Source Zones. I. Analytical Modeling of Source Strength Functions and Plume Response., *Journal of Contaminant Hydrology* 78 (2005) 259-280
- Gao, Hongze. 2011. Groundwater Modeling for Flow Systems with Complex Geological and Hydrogeological Conditions. *Procedia Earth and Planetary Science* 3 (2011)23-28

- Holder, A. W., Bedient, P.B., and Dawson, C.N. 1999. FLOTRAN, A Three-Dimensional Ground Water Model, with Comparisons to Analytical Solutions and Other Models. *Advances in Water Resources* 23 (2000) 517-530
- Kemblowski, M.W., and C.Y. Chiang, 1990, Hydrocarbon thickness fluctuations in monitoring wells, *Groundwater*, 28:244-252
- Koussis, A., Pasmajoglou, and S., Syriopoulou, D., 2002. Modelling Biodegradation of Hydrocarbons in Aquifers: When is the use of the instantaneous reaction approximation justified?, *Journal of Contaminant Hydrology* 60 (2003) 287 – 305
- Mao, X., Prommer, H., Barry, D.A., Langevin, C.D., Panteleit, B., and Li, L., 2004. Three Dimensional Model for Multi-Component Reactive Transport with Variable Density Ground Flow. *Environmental Modelling & Software* 21 (2006) 615-628
- Marinelli, F. and D.S. Durnford.1996.LNAPL Thickness in Monitoring Wells Considering Hysteresis and Entrapment. *Ground Water*. V.34, No.3,405-414, May-June
- van Genuchten, M.T., A closed form of equation for predicting the hydraulic conductivity of unsaturated soils: *Soil Science Society of American Journal*, 44, 489-898